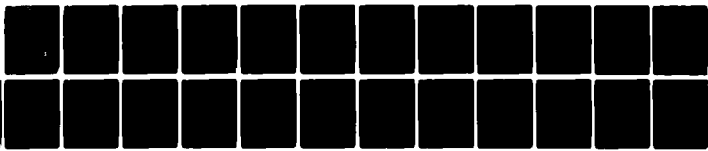


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Auger Lineshapes of Solid Surfaces - Atomic, Bandlike
or Something Else ?

by

Brett I. Dunlap, Fred L. Hutson, and David E. Ramaker

Prepared for Publication

in the

Journal of Vacuum Science and Technology

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Washington, D.C. 20052

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These lineshapes exhibit a wide range of localization consistent with the model.

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Auger Lineshapes of Solid Surfaces - Atomic
Bandlike or Something Else?

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Abstract

A simple model is presented to predict the level of localization (i.e., localization onto an atomic, bonding lobe, molecular, or band orbital) of the two and three hole final states in Auger lineshapes. In the spirit of the Hubbard model, the extent of localization is predicted from the one- and two-center Coulomb interaction potentials and the relevant valence bandwidths. Results from the model are compared with experiment for the N KVV lineshape from NaNO_3 , and the S and Si L_{23}^{VV} lineshapes from Li_2SO_4 and SiO_2 . These lineshapes exhibit a wide range of localization consistent with the model.

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Often the core-valence-valence (CVV) Auger lineshapes can be successfully interpreted as the self-convolution of the valence band density of states,¹ particularly for conductors with wide valence bandwidths Γ . Matrix element effects² and initial state screening³ can alter this picture to some extent. If the lifetime of the core hole is short enough, the Auger electron can interact with the particles and fields present during the creation of the core hole.⁴⁻⁶ Near threshold, when the kinetic energy of the Auger electron is low, post-collision interactions can effect the lineshape.⁷ A more detailed and balanced discussion of these and other factors affecting Auger lineshapes in solids has been givenⁱⁿ the excellent review by Fuggle.⁸

The most dramatic departures from the valence-band self-convolution lineshape occurs if two (or more) holes are trapped locally in their mutual Coulomb repulsion.⁹⁻¹¹ For example, two conduction band holes in the final state of the Auger process are trapped rendering the $L_3M_{45}M_{45}$ Auger lineshape atomic-like for the elemental solids Cu, Fe, Ga and Ge¹². Similarly, a valence hole created via shakeoff during the initial state ionization process can become trapped locally due to the core-valence Coulomb repulsion U_{cv} leading to a shake-Auger satellite contribution to the total Auger lineshape. The three-hole final state of the shake-Auger process may be localized even though the two-hole final state from the normal Auger process is not because of the increased Coulomb repulsion of the 3-holes.

In the Cini-Sawatzky⁹⁻¹⁰ (CS) model of the Auger process in elemental solids, two parameters determine the degree of

localization of the CVV two-hole final state. Since inter-atomic Auger matrix elements are negligible¹³, except where intra-atomic transitions are blocked¹⁴, the Auger process picks out a local density of states (DOS), i.e., the Auger intensity is proportional to the probability that the two holes are local to the atom with the initial core hole. This local DOS experiences an effective one-center Coulomb repulsion U . The energy of this state is degenerate with that of two delocalized band electrons if $U < \Gamma$, and thus to a good approximation the Auger lineshape is quasiatomic provided $U > \Gamma$ and a self-convolution of the valence band provided $U < \Gamma$. In regions where $U \approx \Gamma$ both atomic and bandlike contributions are evident in the lineshape; i.e., correlation effects are present.

The CS model has been applied only to mono-elemental solids, primarily metals. Consequently the localization can be described as either atomic or bandlike. A very interesting question arises; are there systems where intermediate levels of localization exist, i.e., localization on some sub-cluster of the system? Some ionic solids contain covalently bonded sub-clusters such as the oxy-anions (e.g., NO_3^- and SO_4^{2-}) where it is easy to envision delocalization within the molecular anions. Recently, we reported Auger contributions resulting from localization onto a Si-O-Si bond orbital cluster in SiO_2 ,¹¹ a covalently bonded system.

We report in this work a summary of studies on the solids LiNO_3 ¹⁵ and Li_2SO_4 ,¹⁶ along with conclusions from our study

in SiO_2 .¹¹ In these systems there are a wide range of possible localized initial and final Auger states. They could involve localization onto an atomic orbital (AO), onto a bonding lobe orbital (LO), onto a subcluster molecular orbital (MO), or delocalized throughout the band orbital (BO). A simple semiempirical model is presented here for determining the extent of localization and its effects on the experimental Auger lineshapes. This model is presented in the next section. Application of this model to the systems under study are presented in Sec. 3.

2. Theoretical Model

For the poly-elemental solids such as those under study, a cluster configuration interaction (CI) approach, such as that described previously by one of us is appropriate.¹¹ The results of that approach and the necessary definitions of the parameters involved is best summarized by presenting a simple two-orbital model problem.

For the moment, we assume the system has two holes present which is appropriate for the initial shake-Auger or final (normal) Auger state assuming an initially closed shell or filled band state (e.g., an insulator). We describe the holes by the one-electron orbitals ϕ_a and ϕ_b and proceed to diagonalize the hamiltonian $H = h_1 + h_2 + r_{12}^{-1}$ (We consider only the singlet spin states and assume $\langle \phi_a | \phi_b \rangle = 0$.)

$$\begin{array}{c}
 \begin{array}{c} \phi_a^2 \\ \phi_b^2 \\ \frac{1}{\sqrt{2}}(\phi_a\phi_b + \phi_b\phi_a) \end{array} \left| \begin{array}{ccc} \phi_a^2 & \phi_b^2 & \frac{1}{\sqrt{2}}(\phi_a\phi_b + \phi_b\phi_a) \\ 2\varepsilon_a + U_{aa} & 0 & H_{ab} \\ 0 & 2\varepsilon_b + U_{bb} & H_{ab} \\ H_{ab} & H_{ab} & \varepsilon_a + \varepsilon_b + U_{ab} \end{array} \right| \quad 1)
 \end{array}$$

where $\epsilon_a = \epsilon_b$ are the one-electron orbital energies (e.g. $\epsilon_a = \langle \phi_a | h | \phi_a \rangle$), $U_{aa} = U_{bb}$ and U_{ab} are the one- and two-center Coulomb repulsion interaction integrals, $\langle \phi_a^2 | r_{12}^{-1} | \phi_a^2 \rangle$ and $\langle \phi_a \phi_b | r_{12}^{-1} | \phi_a \phi_b \rangle$ respectively, and $H_{ab} = \langle \phi_a | h | \phi_b \rangle$ is the hopping matrix element. Clearly if $H_{ab} \ll U_{aa} - U_{ab}$, very little mixing occurs and the hole states ϕ_a^2 , ϕ_b^2 , and $\phi_a \phi_b + \phi_b \phi_a$ essentially diagonalize H , i.e., the orbitals ϕ_a and ϕ_b properly describe the localization of the two holes. If $H_{ab} \gg U_{aa} - U_{ab}$, the mixing of the configurations is complete and the eigenstates are

$$\begin{aligned} 1) \quad & \frac{1}{2} (\phi_a^2 + \phi_b^2 + \phi_a \phi_b + \phi_b \phi_a) = \frac{1}{2} (\phi_a + \phi_b)^2 \\ 2) \quad & \frac{1}{\sqrt{2}} (\phi_a^2 - \phi_b^2) = \frac{1}{\sqrt{2}} [(\phi_a + \phi_b)(\phi_a - \phi_b) + (\phi_a - \phi_b)(\phi_a + \phi_b)] \\ 3) \quad & \frac{1}{2} (\phi_a^2 + \phi_b^2 - \phi_a \phi_b - \phi_b \phi_a) = \frac{1}{2} (\phi_a - \phi_b)^2 \end{aligned} \quad 2)$$

with eigenvalues

$$\begin{aligned} E_1 &= 2\epsilon_a + (U_{aa} + U_{ab})/2 + H_{ab} \\ E_2 &= 2\epsilon_a + U_{aa} \\ E_3 &= 2\epsilon_a + (U_{aa} + U_{ab})/2 - H_{ab} \end{aligned} \quad 3)$$

In this instance the linear combinations $\phi_a \pm \phi_b$ properly describe the localization of the two holes.

We now use an 'Aufbau' principle to determine the extent of delocalization. Consider first the possibility of localization into AO's vs. LO's. The Auger process prepares the holes locally in an atomic orbital, say AO_a^2 . In this instance $H_{ab} = V/2$ (V =bonding-antibonding separation) is the covalent interaction between neighboring atoms (e.g., between the central atom X_p and O_{2p} in XO_n), U_{aa} is the one-center Coulomb repulsion (U_{xx} or

and $U_{oo})/U_{ab}$ is a two center repulsion integral which we approximate by the Klopman approximation:¹⁷

$$U_{ab} = e^2 [R_{ab}^2 + e^4/(U_{aa} U_{bb})]^{-1/2} \quad 4)$$

If $V > U_{xx} - U_{xo}$ the holes delocalize onto the orbital $aAO_x + bAO_o$ which we refer to as a bonding lobe orbital (LO).

A CI involving the LO's proceeds similarly with ϵ_a now the energy of the LO. We assume here that AO_x is an sp^3 (or sp^2 in the case of NO_3) hybrid orbital, thus H_{ab} , U_{aa} and U_{ab} are now the covalent and Coulomb interactions between lobe orbitals.

$$\begin{aligned} H_{ab} &= \gamma/n = a^2 h_{xx'} + b^2 h_{oo'} + 2ab h_{xo'} \\ U_{aa} &= U_{ll} = a^2 U_{xx} + b^2 U_{oo} + 2ab U_{xo} \\ U_{ab} &= U_{ll'} = a^2 U_{xx'} + b^2 U_{oo'} + 2ab U_{xo'} \end{aligned} \quad 5)$$

where n is the number of lobes on the MO cluster. We assume $h_{oo'}$ and $h_{xo'}$ are negligible; $h_{xx'} = 2(\alpha_s - \alpha_p)$, where α_s and α_p are the empirical one-electron atomic s and p orbital binding energies of the central atom.¹⁸ γ can be obtained empirically from the spread in energy of the X s and p orbitals in the O_{2p} bonding band of the system; information which can be obtained from x-ray emission data. If $\gamma > U_{ll} - U_{ll'}$, the holes delocalize onto clusters involving the n LO's on the X atom, $MO = \sum_{i=1}^n c_i LO_i$.

A CI involving MO's on different molecular clusters requires the quantities $H_{ab} = \Gamma/N$, $U_{vv} = (U_{ll} + (N-1) U_{ll'})/N$, and $U_{vv'} = e^2/R$, where Γ is the orbital band width, N is the number of nearest neighbor clusters, R is the X-X' nearest neighbor distance, and U_{vv} and $U_{vv'}$ are the Coulomb interactions between holes on the same and neighboring MO clusters (e.g., XO_n). If $\Gamma > U_{vv} - U_{vv'}$, the holes delocalize in the BO's.

Summarizing the results of the CI approach we have:

$$\begin{array}{lll}
 V < U_{xx} - U_{xo} & \phi \rightarrow AO & \\
 V > U_{xx} - U_{xo} \quad , \quad \gamma < U_{\ell\ell} - U_{\ell\ell'} & \phi \rightarrow LO & 6) \\
 \gamma > U_{\ell\ell} - U_{\ell\ell'} \quad , \quad \Gamma < U_{vv} - U_{vv'} & \phi \rightarrow MO & \\
 \Gamma > U_{vv} - U_{vv'} & \phi \rightarrow BO &
 \end{array}$$

where ϕ describes the appropriate localization of the two holes. By defining the U's appropriate to the 3-hole Coulomb interaction, we can describe the localization in the 3-hole shake-Auger final state. If the U's are defined as a core-valence Coulomb interaction, we can determine the localization of the core-valence state initiating the shake-Auger process.

A quantitative comparison of theory and experiment is made by deriving a theoretical Auger lineshape. The Auger transition energies are given by

$$E_{cnn'} = E_c - E_n - E_{n'} - U_{nn'} \quad 7)$$

where E_c is the core one-electron binding energy and E_n and $U_{nn'}$ are the valence one-electron binding energy and Coulomb interaction appropriate for the extent of localization, i.e., for the atomic, lobal, molecular, or band orbital. Auger intensities are computed from the local AO populations a_{xn}^2 and atomic Auger matrix elements $M_{cxx'}$,

$$I_{cnn'} = a_{xn}^2 a_{x'n'}^2 M_{cxx'} \quad 8)$$

both determined as described previously.¹⁹ The Auger widths are approximated as a sum,

$$\Gamma_{cnn'} = \Gamma_c + \Gamma_n + \Gamma_{n'} + 2K \quad 9)$$

of core Γ_c and valence Γ_n level widths plus a singlet-triplet spin splitting term obtained as described previously.¹⁹

A large contribution (20 to 40%) to the total Auger line-shape results from shake-Augur satellites. These contributions arise from shake-off during the initial core ionization process, the additional valence state hole causing a shift in the Auger energy. The shake-up process (valence excitation instead of valence ionization) is not significant in the insulating systems studied here due to the large band gaps at the Fermi level.²⁰ The probability for shake resulting from core ionization can be determined from the sudden approximation

$$P_n = 1 - \langle \phi_n \phi'_n \rangle^{2N}, \quad (10)$$

where ϕ_n (ϕ'_n) is the unrelaxed (relaxed) orbital describing the proper localization of the valence hole. We approximate eq. (10) with the expression

$$P_n = 1 - (1-a^2 + a^2 (1-P_a)^{1/2N})^{2N}, \quad (11)$$

where a^2 is the local orbital population and P_a the atomic shake-off probability for the atom with the core hole. A comparison of the results using eqs. (10) and (11) for the NH_3 molecule²¹ indicates eq. (11) is a good approximation. The resultant satellite intensity is

$$I_{cs-snn'} = \frac{(N-i)}{N} \frac{P_n}{1-\sum P_n} I_{cnn'}, \quad (12)$$

where $i=1$ if $s=n \neq n'$, $i=2$ if $s=n=n'$ and $i=0$ otherwise. (Eqs. (11-12) correct eqs. (1-2) in ref. 22.) The shift in energy between the parent Auger and shake satellite contributions is approximated by²²

$$\Delta E_{cs-snn'} = U_{cs} - U_{sn} - U_{sn'} = U_{cs} - U_{snn'} + U_{nn'} \quad (13)$$

where the U 's must be evaluated with the properly localized orbitals, and the sum of pairwise potentials has been assumed.

3. Results and Discussion

As seen from Table I, $U_{xx} - U_{xo}$ is generally less than 10eV. The X-O covalent interaction V is ≈ 10 -12eV, for the systems under study,²³ thus delocalization from the central atom X is expected. On the other hand, $\Gamma' (< U_{vv}, \text{ for } Li_2SO_4 \text{ and } NaNO_3)$ is less than $U_{vv} - U_{vv'}$, ($U_{vv'} \approx 3\text{eV}$), thus delocalization from the anion is not expected. However, if two holes are created in adjacent Si-O-Si lobes, they can delocalize ($U_{\lambda\lambda'}(\text{adjacent}) - U_{\lambda\lambda}$ (non-adjacent) $< \gamma = \Gamma'$). Thus, the focus of this discussion is localization on a lobe verses delocalization onto the molecular anion XO_n , or throughout the system for SiO_2 . It is evident from Table I that two holes will remain localized on a Si-O-Si lobe ($U_{\lambda\lambda} - U_{\lambda\lambda'} > \gamma$); two holes will delocalize onto the NO_3 molecular anion ($U_{\lambda\lambda} - U_{\lambda\lambda'} < \gamma$). The situation is unclear in SO_4 since $U_{\lambda\lambda'} - U_{\lambda\lambda} \approx \gamma$; however, we will proceed to use SO_4 MO's. Therefore, the two hole final state will be described by the XO_n cluster MO approach for oxyanion systems and by the Si-O-Si bond orbital approach in SiO_2 . Local Si-O-Si and non-local Auger contributions (correlation effects) should be seen in SiO_2 , only NO_3 MO contributions will be seen in NO_3 . Large correlations effects should be present in SO_4 , however the local and non-local contributions will not be resolved since $U_{\lambda\lambda} - U_{\lambda\lambda'} \approx \gamma$; thus they will not significantly alter the normal Auger lineshape.

The shake-Augur satellites follow a similar trend. First, note that because of the size of U_{cv} , the shake hole cannot get off of the oxyanion or off the Si-O-Si bond orbital. (If the shake hole could delocalize, all shake satellites would be

absent from the Auger lineshape.) The three-hole final state resulting from the shake - Auger process has a larger Coulomb interaction energy, hence localization and correlation effects are expected to be more important. As revealed in Table I, however, even the three holes should delocalize throughout the NO_3 anion; little correlation effects are expected since

$U_{\text{xx}} - U_{\text{xx}}'$ and $U_{\text{xx}}' - U_{\text{xx}}'' < \gamma$. In SO_4 , $U_{\text{xx}} - U_{\text{xx}}' > \gamma \approx U_{\text{xx}}' - U_{\text{xx}}''$ thus one might proceed with a SO_4 MO picture for the 3-hole state, but large correlation effects should again be expected. In SiO_2 $U_{\text{xx}} - U_{\text{xx}}'$ and $U_{\text{xx}}' - U_{\text{xx}}'' > \gamma$ so the Si-O-Si LO gives the proper description of shake-Augger satellites.

The upper set of curves in Figs. 1-2 compare experimental and total theoretical N KVV LiNO_3 and S L_{23}VV Li_2SO_4 Auger lineshapes respectively. The N lineshape was obtained via x-ray excitation, the S by electron excitation; both were background subtracted and loss deconvoluted by a method described elsewhere.²⁴ The middle curves compare the separate Auger and shake-Augger theoretical contributions, the latter 35% for N and 34% (including Coster-Kronig) for S of the total as determined from eq. (11). These curves have been obtained using eqs. (6) through (13) and NO_3 and SO_4 MO energies and populations as derived and reported elsewhere.¹⁵⁻¹⁶ The total theoretical lineshape was normalized and shifted in energy Δ for principle peak alignment with the experiment. The required energy shifts Δ (+3eV and +2eV respectively) may be attributed to charging of the insulating samples and thus this absolute energy shift

is not a good test for correlation effects in the two-hole state. The lower curves compare the theoretical shake-Augger lineshape with the difference between the total experimental and the theoretical normal Auger lineshapes; the latter may be referred to as the 'experimental' shake-Augger lineshape. Differences between the theory and experiment in the upper and lower curves (by definition the differences are the same) are largest at the higher energies. These may be attributed to damage of the sample since in both NO_3 and SO_4 the higher energy region grows with electron beam exposure. Note, as one might expect, more structure is seen in the shake-Augger than in the normal Auger lineshape.

We focus our attention on the lower curves of Fig. 1-2 and the shift δ required to bring the theoretical and "experimental" shake lineshapes into alignment. This additional shift $\delta = -1\text{eV}$ for NO_3 may be regarded as an adjustment in $\Delta E_{\text{CS-SVV}}$ (a relative energy shift between the Auger and shake-Augger); we can allow this flexibility due to the approximate nature of eq. (13). However, the $\delta = +6\text{eV}$ for SO_4 is larger than the uncertainty in eq. (13), and we attribute it to the large correlation effects expected in the three-hole final states of SO_4 .

Assuming the SO_4 MO's describe the proper localization, eq. (13) gave $\Delta E(\text{MO}) = -8\text{eV}$. If we assume instead that the LO's are more proper, we might expect a shake-Augger contribution at each level of localization; at $\Delta E(\text{lll}) = -17\text{eV}$, $\Delta E(\text{lll}') = -7\text{eV}$, and $\Delta E(\text{lll}'') = -2\text{eV}$. However, the lll contribution is forbidden by the Pauli principle, and the lll' contribution is reduced in

magnitude by matrix element¹¹ and statistical (the $(N-i)/N$ factor in eq. (12)) effects. Thus, we might expect the dominant shake contribution at $\Delta E = -2\text{eV}$ which accounts for the δ shift of $+6\text{eV}$. We conclude the LO gives the more proper localization for the SO_4 three hole final state.

A similar comparison of theory and experiment for the Si $L_{23}\text{VV}$ and O KVV lineshapes in SiO_2 have been given previously.¹¹ Significant correlation effects were evident in these lineshapes already in the two-hole final state as expected from the data in Table I.

In conclusion, it is clear intermediate levels of localization are evident in Auger lineshapes in both the two- and three-hole final states. Our simple model as outlined above is helpful in understanding and predicting the extent of this localization.

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TABLE I. Summary of covalent and Coulomb interactions in
 NO_3^- , SO_4^{2-} , and SiO_2 ^a

<u>Interaction</u>		NO_3^-	SO_4^{2-}	SiO_2
γ^b		9	5	4
U_{xx}^c		12	12	9
U_{xo}^d	eq. (4)	9	8	7
U_{oo}^d	eq. (4)	6	6	5
$U_{\lambda\lambda}^d$	eq. (5)	12	12	11
$U_{\lambda\lambda'}^d$	eq. (5)	8	7	5
$U_{vv} = (U_{\lambda\lambda} + (N-1)U_{\lambda\lambda'})/N$		9	9	6
U_{cv}^e		13	10	9
$U_{\lambda\lambda\lambda} = 3U_{\lambda\lambda}$		36	36	33
$U_{\lambda\lambda\lambda'} = U_{\lambda\lambda} + 2U_{\lambda\lambda'}$		28	26	21
$U_{\lambda\lambda'\lambda''} = 3U_{\lambda\lambda'}$		24	21	15

^aAll quantities (in eV) evaluated assuming the electron population on the central atom a^2 is .38, .25, and .25 respectively for N, S, and Si. We assume $a^2 + b^2 = 1$ and utilize the zero differential overlap approximation. All numbers have uncertainties of the order ± 1 eV.

^bEvaluated empirically from an analysis of x-ray emission and photoemission data (11, 15-16) and from $2(\alpha_s - \alpha_p)a^2$. Agreement to within 1 eV is obtained.

^c $U_{nn} = F_{nn}^0 - r_{nn}$ where F^0 is the Slater integral tabulated by Mann²⁵ and r is a relaxation energy²⁶ estimated to be 6, 6, 1 and 1 eV for N, O, S, and Si. $U_{oo} = 15$ eV

TABLE I (continued)

^dEvaluated using $R_{xo} = 1.2, 1.4, \text{ and } 1.6$, $R_{oo} = 2.1, 2.4,$
and 2.6 \AA respectively for NO_3 , SO_4 , and SiO_2

^e $U_{cv} = a^2 U_{cx} + b^2 U_{co}$ where U_{cx} is determined using the
equivalent cores approximation²⁶.

Figure Captions

Fig. 1

Upper curves: the total experimental (solid line) and theoretical (dotted line) N KVV Auger lineshape for NaNO_3 . The theoretical lineshape has been normalized and shifted by $\Delta = 3\text{eV}$ to align with the principle experimental peak.

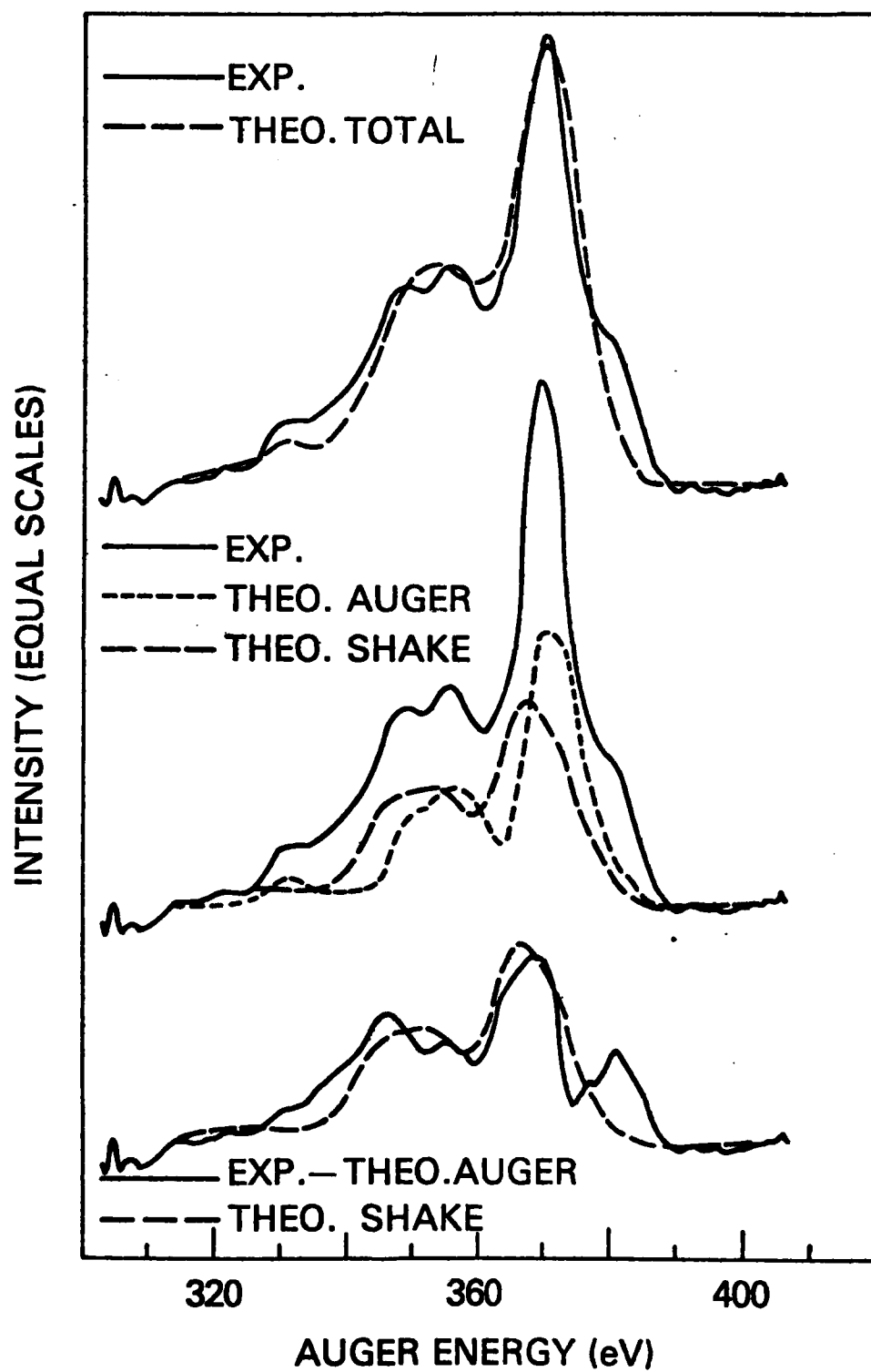
Middle curves: the normal Auger (solid) and shake-Auger (dotted) contributions to the total Auger lineshape.

Lower curves: the "experimental" (solid) and theoretical (dotted) shake-Auger lineshape. The "experimental" was obtained by subtracting the theoretical normal Auger lineshape from the total experimental lineshape. The theoretical lineshape was shifted by $\delta = -1\text{eV}$ for better alignment.

Fig. 2

Same as Fig. 1 for Li_2SO_4 , except $\Delta = +2\text{eV}$ and $\delta = +6\text{eV}$.

NO₃⁻ N kVV

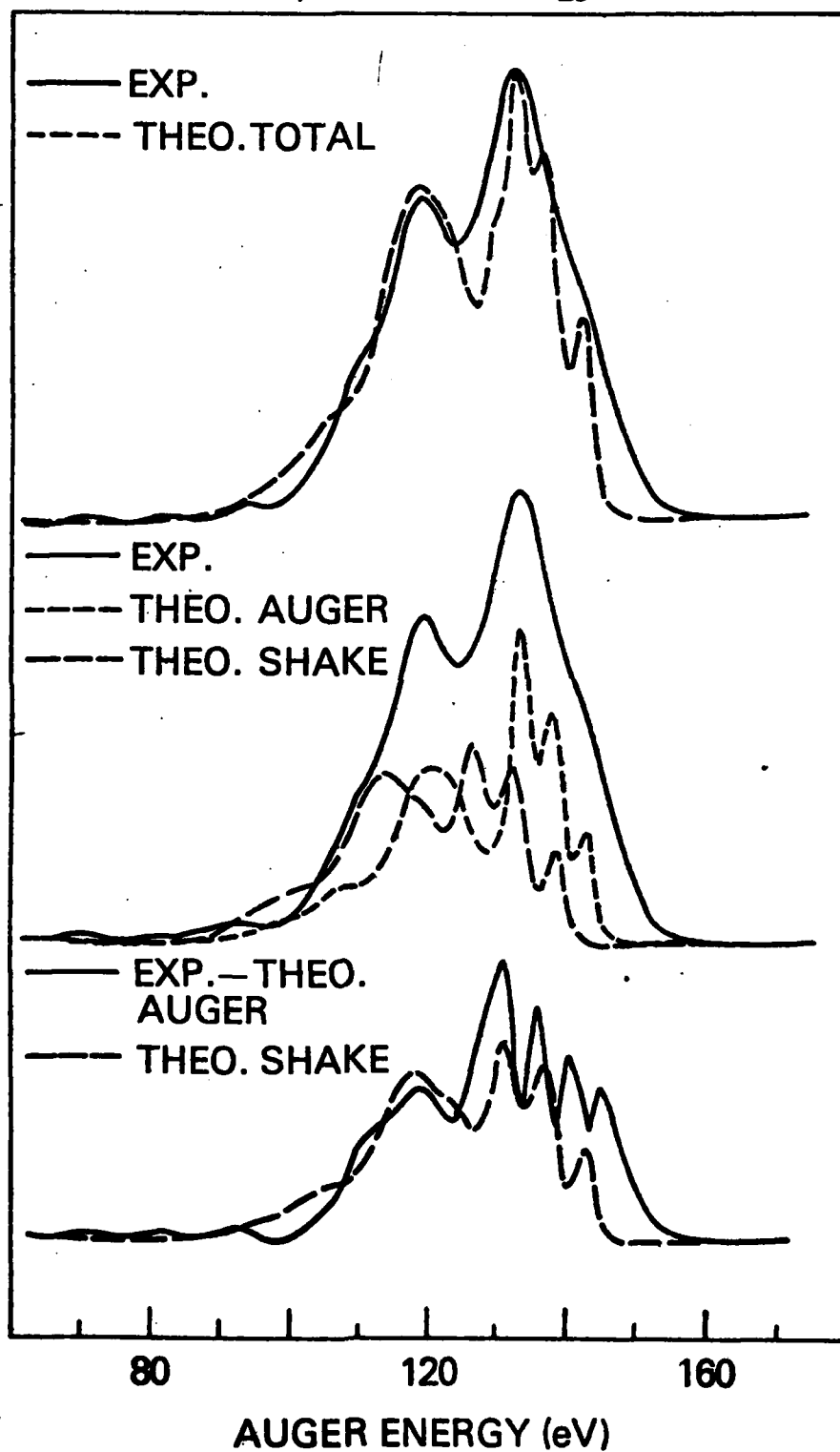


$\text{SO}_4^{=}$

S

L_{23}VV

INTENSITY (EQUAL SCALES)



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